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(54) CASING PAPER HAVING ALKALI RESISTANCE

(71) We, C. H. DEXTER LIMITED, a body corporate organised under the laws of the United Kingdom, of Chirnside, Duns, Berwickshire, Scotland TD11 3JU, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The present invention relates to casing paper, which may be used for the production of packaging for meat products such as sausage.

15 Casing paper is commonly manufactured from paper webs of relatively strong, high-tenacity natural fibres, such as abaca, sisal or flax. The paper web is saturated with a dilute viscose solution, for example a solution obtained by diluting a solution containing 7% by weight of cellulose (as cellulose xanthate) and 6% by weight of sodium hydroxide to a 1% cellulose content. The viscose-saturated web is dried and the cellulose in the viscose is then regenerated 20 by passing the web through an acidic regenerating bath containing, for example, a 1—8% aqueous sulphuric acid solution. The web is then washed free of acid and dried to produce a paper web impregnated 25 with acid-regenerated cellulose. This casing paper is then generally formed into rolls ("master rolls").

30 casings for the packaging of processed meats, e.g. sausage, may be manufactured from the casing paper by cutting it into strips which are then folded to form tubes. The tubes are saturated with an alkaline viscose solution, containing, for example, 7% by weight of cellulose and 6% by weight of sodium hydroxide. The cellulose in the 35 viscose is then regenerated by means of an acidic regenerating bath containing, for example, dilute sulphuric acid and possibly such salts as sodium sulphate or ammonium sulphate. The tube is then passed through 40 one or more baths in order to wash out the acid and the salts.

45 If desired, the tube may be passed

through an aqueous bath which contains a plasticizer, e.g. glycerine, for the regenerated cellulose. The tube is dried by passing it through a heated chamber (the tube being in an inflated state) to give a cellulosic tubing which has embedded therein a paper web. This tubing may then be stuffed with a processed meat product under pressure. A process of this type is described in detail in United States Patent No. 3,135,613.

50 The purpose in treating the initial paper web with dilute viscose solution, followed by regeneration, is to provide the web with strength and structural integrity so that it may withstand the treatment with the highly caustic viscose solution used in the formation of the casing tubes. The amount of cellulose in the casing paper is, in fact, comparatively low; thus, the casing paper may have a typical basis weight (weight per unit area) of 20 grams/m², of which the cellulose accounts for 0.6 g/m², compared with the material of the casing tubes which may have a typical basis weight of 70—80 g/m², of which 50—60 g/m² may be accounted for by the cellulose. However, despite the initial treatment with viscose, the treatment with the highly caustic viscose solution used in the formation of the casing tubes will inevitably entail a certain degree of softening and weakening of the web. This imposes a limit on the production speeds if difficulty in handling the webs and possible breakdowns in production are to be avoided. There is accordingly a need in the art for casing paper having an improved alkali resistance in order to permit higher production speeds in the manufacture of the casing tubes.

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In United States Patent 3,378,379, there is disclosed a tubular regenerated-cellulose casing for dry sausage, which casing is provided with a coating comprising a cationic thermosetting resin bonded to the inside wall thereof. The patent suggests that polyethylene imine may also be employed for this coating, although this material is

not, in fact, a cationic thermosetting resin. The purpose of the inner coating is to improve the adhesion of the sausage casing to a dry sausage product despite any shrinkage which may occur when the dry sausage product is processed and dried in the casing over a prolonged period of time. It should be noted, however, that in the aforesaid process it is not the casing paper as such which is treated with the thermosetting resin, but the tubular casing material. In the embodiment illustrated in U.S. Patent 3,378,379, the cationic thermosetting resin is applied to the inner surface of the casing tube after the application of glycerine and before the casing is dried, in an inflated state, in a heated chamber.

Another problem recognised in U.S. Patent No. 3,378,379 is the variation in extensibility in the transverse direction exhibited by casing paper strips cut from different parts of the master roll. This can cause variation in the properties of the final casing tubes, which may therefore be unsatisfactory to the meat packager, for whom dimensional stability in the product is of commercial importance. To meet this problem it is suggested in the aforesaid U.S. Patent that a cationic thermosetting resin (e.g. a reaction product of epichlorohydrin and a polyamide, a modified melamine-formaldehyde resin or a modified urea-formaldehyde resin) may be employed as the bonding agent in the casing paper, instead of the commonly employed acid-regenerated viscose. The cationic thermosetting resin is employed in an amount of at least 0.5% by weight based upon the dry weight of the impregnated fibrous web. The resin may be incorporated into the fibrous web by adding the resin to the fibrous slurry prior to forming the fibrous web. Alternatively, the formed fibrous web may be impregnated with the resin by passage through an aqueous solution of said resin. The said U.S. patent also discloses the use of the thermosetting resin in combination with viscose which is not regenerated with an acid; however, in the latter case the viscose may be auto-regenerated by storing the web for a sufficient period.

In United Kingdom Patent Specification 1,091,105 there is described a process in which casing paper is produced by incorporating into a paper web an alkaline-curing resin such as polyethylene imine or a polymeric reaction product of epichlorohydrin and a polyamide. The use of the alkaline-curing resin in place of the customary treatment with dilute viscose is said to result in a casing paper which has more uniform characteristics across its width and which results in a casing having improved burst strengths. However, it has now been found that the casing paper so

produced has an alkali resistance which is insufficient to permit sufficiently high production speeds for the commercial manufacture of the casing tubes.

It is an object of the present invention to provide a process for the production of casing paper having a good alkaline wet strength and from which casing tubes may be produced using high-speed commercial processes.

Accordingly, the present invention provides a process for the production of casing paper (as hereinafter defined), which process comprises forming a fibrous paper web, treating the fibrous paper web with a dilute viscose solution and subsequently regenerating the cellulose in the viscose by means of an acid, wherein the fibres of the paper web are treated with a polyalkylene imine. Preferably, this treatment is carried out prior to, or simultaneously with, the treatment with the said dilute viscose solution.

The present invention also provides casing paper (as hereinafter defined) which comprises a fibrous web impregnated with cellulose and having incorporated therein a polyalkylene imine. The invention also provides casing material for processed meat products being casing material manufactured from the casing paper of this invention, in particular by a process comprising the application of a highly alkaline viscose solution and subsequent acid regeneration.

The expression "casing paper" as used herein refers to a fibrous paper-like material which has not yet been treated with a highly alkaline viscose solution. It will be appreciated from the initial discussion of the prior art that such highly alkaline (or caustic) viscose solutions (as are customarily used in the manufacture of the final food-casing materials) are clearly distinguished in the art from the dilute viscose solutions employed to impart strength and structural integrity to the paper web.

The preferred polyalkylene imine is polyethylene imine (PEI). Polyethyleneimine is a water-soluble, cationic homopolymer which may be synthesised by acid-catalysed polymerisation of ethyleneimine. It is known in the paper-making art as a retention aid to prevent short fibres passing through the papermaking wire.

It has been found, for example, that there is a synergistic effect between polyethylene imine (PEI) and the viscose, which can result in a marked improvement in the alkaline wet strength of casing paper produced according to the present invention, whilst the viscose absorbency of the casing paper remains satisfactory. It has been found that PEI, when used in the

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absence of any other binding agent, provides virtually no increase in the wet strength of the paper web. Moreover the attainment of such an improved alkaline wet strength is particularly surprising since PEI can be decomposed, under certain conditions, by acids.

Normally, the amount of polyalkylene imine added will be 0.1 to 2%, and preferably 0.2 to 1%, by weight of the fibrous web, on a dry weight basis.

The viscose is generally added to the fibrous material in amounts which are customary in the art for the production of 15 casing papers containing acid-regenerated viscose.

The polyalkylene imine may be added to the fibres during the paper-web-making process or may be applied to the fibrous web as made. Conveniently, however, the polyalkylene imine may be included in the dilute viscose solution itself.

In a particularly preferred embodiment of the present invention, the fibres of the paper web are also treated with a cationic, thermosetting, epihalohydrin-containing resin. Preferably, the fibrous web is treated with both the polyalkylene imine and the said epihalohydrin-containing resin prior to 25 or simultaneously with the treatment with the viscose solution. It has been found that the alkali resistance of casing paper prepared by this method can be significantly higher than would be expected from results obtained by treatment with either of the treating agents alone.

Normally the amount of the said epihalohydrin-containing resin will be 0.1 to 4%, and preferably 0.25 to 2%, by weight of the fibrous web, on a dry weight basis.

Preferably, the said cationic, thermosetting resin is an epichlorohydrin-containing resin.

A preferred class of cationic, thermosetting resins are the water-soluble polyamide-epichlorohydrin resins (PAE), such as those prepared by the reaction of epichlorohydrin with polyamides derived from polyalkylene polyamines (e.g. diethylene triamine or tetraethylene pentamine) and saturated or unsaturated aliphatic or aromatic polycarboxylic acids containing 3 to 10 carbon atoms (e.g. adipic, itaconic, or succinic acid). Resins of this type are described in U.S. Patents No. 2,926,116, No. 2,926,154 and No. 3,125,552.

In U.S. Patent 3,535,288 there are disclosed suitable resins that are derived from epichlorohydrin and polyamides that are the reaction products of certain amino polycarboxylates and derivatives thereof, especially ethylenediaminetetraacetic acid or diethylenetriamine pentaacetic acid, and polyalkylene polyamines, especially pentaethylenehexamine.

Suitable polyamide-epichlorohydrin resins are also disclosed in U.S. Patent 3,526,608. Here the polyamides are obtained from the reaction of polyalkylene polyamines, and either iminodiacetic acid, N,N'-piperazinediacetic acid, N-alkyl-iminodiacetic acids, N,N'-dialkylethylene-diamine-N,N'-diacetic acids, or their corresponding lower alkyl esters. Preferred polyalkylene polyamines are diethylenetriamine, triethylenetetramine, and tetraethylenepentamine and mixtures of these polyamines.

The resins disclosed in U.S. Patent 3,565,754 are provided by reacting epichlorohydrin with polyamides derived from nitrilotriacetic acid and polyalkylene polyamines containing two primary amine groups and at least one secondary amine group in which the nitrogen atoms are linked together by groups having the formula $-\text{C}_n\text{H}_{2n}-$ where n is a small integer generally having a value of 2 and the number of such groups in the molecule ranges from 2 to 19 and preferably up to 6. The nitrogen atoms may be attached to adjacent carbon atoms in the group $-\text{C}_n\text{H}_{2n}-$ or to carbon atoms further apart, but not to the same carbon atom.

As disclosed in U.S. Patent 3,816,556, water-soluble, cationic, thermosetting polyamide-epichlorohydrin resins can be converted into polysalts by reaction with certain anionic, water-soluble polyacrylamides. Such polysalts are useful in this invention.

Other epichlorohydrin-containing resins which can be used include the reaction products of epichlorohydrin with polymers derived from polyacrylamide and polyamines such as ethylene-diamine (U.S. Patent 3,507,847); with hydrolysed polyvinylimidazoline (U.S. Patent 3,640,936); with polyaminepolyamide polymers derived from certain heterocyclic dicarboxylic acids, aminocarbonyl compounds, di- or polyalkylene polyamines and epichlorohydrin (U.S. Patent 3,761,350); and with polyethyleneimine (U.S. Patent 3,520,774).

The fibrous webs used in making casing paper are conventionally composed of natural vegetable fibres of pure cellulose and are preferably composed of long light-weight nonhydrated fibres of the Musa type, particularly hemp fibres of the Manila or abaca hemp variety. Webs made from this material are generally soft porous papers of uniform texture and thickness and have for some time found wide acceptance as the primary fibre component of the fibrous base webs used in casing manufacture.

Prior to its impregnation with a caustic viscose solution or the like in order to form the final casing material, the casing paper

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may be treated in order to improve its absorbency yet further. One preferred method is to subject at least one side of the web to a corona discharge treatment at an energy density of at least 0.5 Watt-min/ft² of web surface. The usual level will exceed 1.5 Watt-min/ft² and is preferably 5 to 40 Watt-min/ft². This treatment is described and claimed in United Kingdom Patent Application No. 40210/76, Serial No. 1,517,489.

10 The present invention is illustrated by the following Examples.

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Handsheets were made in the laboratory using an abaca stock. A 0.1% solution of Polymin P (the trade name of a polyethylene imine marketed by BASF, Germany) ("Polymin" is a trade mark) was added to the sheet mould in an amount sufficient to provide 1% of polyethylene imine in the resultant handsheets, on a dry weight basis. The sheets were then saturated with a dilute viscose solution and then subjected to the acid-regeneration process. The sheets were then tested for their wet tensile strength and alkaline wet tensile strength on Instron (trade mark) and Scott tensile testers respectively. For testing alkaline wet tensile strength, the sheets

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were saturated with a 6% caustic soda solution.

The results are shown in Table 1 below.

Example 2.

Handsheets were made in the laboratory using an abaca stock, but no polyethylene imine was added to the mould. The handsheets so produced were then impregnated with Polymin P and with viscose using a laboratory sizepress, to give approximately a 2% pickup of the Polymin P and the viscose. The said additives were present in the saturating bath of the sizepress in the ratio of 10 parts by weight dry Polymin P to 90 parts dry viscose. The treated handsheets were then subjected to the acid regeneration process and were subsequently tested for their wet tensile strength and alkaline wet tensile strength, as described in Example 1.

For comparison purposes, handsheets were made that were treated with either viscose only or Polymin P only, and these were tested as described above.

The results are shown in Table 1 below.

In Table 1 the wet tensile and alkaline wet tensile strengths are averages of a number of test results. In the cases of the viscose only and of Example 1 results are presented for two different sheet weights.

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TABLE 1

Treatment	Sheet Weight (gsm)	Wet Tensile (gm/25 mm)	Alkaline Wet Tensile (gm/15 mm)
Polymin P only	24.4	60	10
Viscose only and acid regeneration	26.4	920	15
	27.3	950	60
Example 1	25.0	800	210
,, ,	27.5	1070	240
Example 2	24.6	990	310

Example 3.

Non-viscose treated casing paper base was manufactured on a small-scale (24 inches wide) paper machine. The base stock was prepared by desizing a known weight of abaca pulp at a consistency of approximately 4%, and adding to the base stock various quantities of additive selected from Polymin P, Kymene 557 (the trade name of a water-soluble epichlorohydrin-polyamide resin marketed by Hercules Powder Company) ("Kymene" is a trade mark) and mixtures thereof.

The pre-treated base paper was then converted to casing paper on a commercial continuous-process unit, the base paper being first saturated with a viscose solution in a sizepress. After partial drying of the base paper sheets, the viscose was regenerated in an acid press, the sheets being subsequently washed to remove any excess chemicals, dried and wound up. The amount of viscose applied to the sheet in the process was approximately 2% by weight of the original sheet.

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The finished casing papers were then

tested for conventional wet tensile strength, this being measured on strips of the paper 25 mm wide which were saturated with water. The alkali resistance of the casing 5 papers was measured by recording the tensile strength of wet strips, 15 mm wide, after soaking them for 20 minutes in a 6% solution of sodium hydroxide (the results being designated as the alkaline wet tensile 10 strength). The absorbency of the sheets was also measured as the time taken for water to climb 1 inch up a vertical strip of the casing 15 paper. A high absorbency value will indicate that an undesirable sizing effect had taken place, which would interfere with the resaturating of the casing paper with viscose as effected during the customary manufacture of casing tubes or skins.

The results obtained are shown in Table 2 below. The tensile strengths are quoted both as measured (for an average of seven tests for each sample) and also as corrected to a constant basis weight in order to allow direct comparison of the effects to be observed. This, of course, depends upon the assumption that strength is directly proportional to weight, an assumption which may not be perfectly correct, but which is sufficiently valid for the present purposes.

Also quoted is the ratio of the wet strength initially retained after the 20 minutes' soak in alkali. This helps in assessing the true alkali resistance of the sheets, but should be considered in conjunction with the actual strength figures.

TABLE 2

Pre-Treatment of Base (expressed as dry wt. of additive on dry wt. of fibre, as percentage). (All webs subsequently viscose treated)	Basis Wt. (gsm)	Wet Tensile Strength (gms/25mm)	Wet Tensile Strength converted to 21 gsm B.W.	Alkaline Wet Tensile Strength (gms 15 mm)	Alkaline Wet Tensile Strength converted to 21 gsm B.W.	% Alk. W.T.	Absorbency (secs)
No Pre-treatment	23.40	1391	1248	317	284	22.8	17
	19.38	1255	1360	228	247	18.1	11
	19.13	1086	1192	203	220	18.7	10
	22.00	1219	1164	299	285	24.5	12
	22.90	1294	1187	342	314	26.4	12
	22.03	1376	1312	215	205	15.6	10
	22.46	1361	1273	254	237	18.7	12
Polyamide- epichlorohydrin (Kymene 557)	1.0% 2.0%	21.00 22.22	1484 1646	1484 1536	242 269	242 254	16.3 16.3
Polyethyleneimine (Polymin P)	0.25% 0.5%	20.05 23.67	1238 1454	1296 1290	250 346	262 307	20.2 23.8
Kymene 557 / Polymin P	0.25/0.25% 0.5/0.5%	21.87 21.11 22.27 26.74	1359 1489 1496 1948	1367 1481 1411 1530	346 392 433 529	332 289 408 415	25.5 26.3 28.9 27.2

From the results given in Table 2, the following conclusions can be drawn. The use of polyamide-epichlorohydrin resin with regenerated viscose provides an increase in wet strength at an addition level of 1%—2% by weight, but appears to have no significant effect on the alkaline wet strength. The alkaline wet strength is increased with increasing levels of polyethylene imine when this is employed alone in the base sheet.

A combination of a polyamide-epichlorohydrin resin and polyethylene imine causes an increase in wet tensile strength similar to that obtained by pretreating the base with polyamide-epichlorohydrin resin alone, but brings about a very marked improvement in alkaline wet tensile strength at all levels used. However, the addition of 0.5% to 1% polyamide-epichlorohydrin resin in combination with 0.5% of polyethylene imine (by weight of the base web, on a dry weight basis) appears

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to be a particularly efficient amount, based on considerations of both performance and addition levels.	appendant to claim 6 wherein the fibrous web is treated with the polyalkylene imine and the said epihalohydrin-containing resin simultaneously with the dilute viscose solution.	55
5 No detrimental effect on absorbency appears to be caused by any of the additions made.	11. A process according to any of claims 8 to 10 wherein the said epihalohydrin-containing resin is incorporated into the fibrous web in an amount of 0.1 to 4% by weight of the fibrous web, on a dry weight basis.	60
10	12. A process according to claim 11 wherein the said epihalohydrin-containing resin is incorporated into the fibrous web in an amount of 0.25 to 2% by weight of the fibrous web, on a dry weight basis.	65
15	13. A process according to any of claims 8 to 11 as appendant to claim 5, wherein the said epihalohydrin-containing resin is a polyamide-epichlorohydrin resin.	70
20	14. Casing paper (as hereinbefore defined) which comprises a fibrous web impregnated with cellulose and having incorporated therein a polyalkylene imine.	75
25	15. Casing paper according to claim 14, wherein the polyalkyleneimine is polyethyleneimine.	80
30	16. Casing paper according to claim 14 or 15 which also has a cationic, thermosetting, epihalohydrin-containing resin incorporated therein.	85
35	17. Casing paper according to claim 16, wherein the said epihalohydrin-containing resin is a polyamide-epichlorohydrin resin.	90
40	18. A process for the production of casing paper, being a process substantially as hereinbefore described in Example 1, 2 or 3.	95
45	19. Casing paper whenever prepared by a process according to any one of claims 1 to 13 and 18.	100
50	20. Casing material for processed meat products, being casing material manufactured from casing paper according to any of claims 14 to 17 and 19.	
50	21. Casing material according to claim 20, the manufacture of which comprised the application to said casing paper of a highly alkaline viscose solution and subsequent acid regeneration.	
10. A process according to claim 8 as appendant to claim 7, wherein the fibrous web is treated with the polyalkylene imine and the said epihalohydrin-containing resin prior to the treatment with the dilute viscose solution.	For the Applicants, CARPMAELS & RANSFORD, Chartered Patent Agents, 43 Bloomsbury Square, London W.C.1.	